

The Crystal Structure of K_2SeO_4

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Potassium selenate crystallizes in the orthorhombic space group $Pnam$ with $a=7.661 \pm 0.004$, $b=10.466 \pm 0.008$, $c=6.003 \pm 0.003$ Å. Refinement of the structure, which is isomorphous with β - K_2SO_4 , has been carried out by the method of least squares with anisotropic vibrational parameters. R decreased to 4.8% for 334 independent reflexions measured on an automatic diffractometer. The structure is built of fairly regular SeO_4^{2-} tetrahedra, with a mean vibrationally-corrected Se–O bond length of 1.648 ± 0.010 Å, and K^+ cations in two different oxygen environments.

Introduction

The crystal structure studies of the orthoselenates in the literature are mostly limited to the determination of the crystal data, which indicate, however, the important fact that their structures are generally isomorphous with those of the corresponding sulphates (Aurivillius & Malmros, 1961; Gattow, 1960, 1962; Kokkoros, 1938; Madar, 1960; Pistorius, 1966; Pistorius & Pistorius, 1962). Only a few structure analyses have been completed: H_2SeO_4 (Bailey & Wells, 1951), Na_2SeO_4 (Náray-Szabó & Argay, 1963) and $Cu(NH_3)_2SeO_4$ (Morosin, 1969). There is also the structure determination of Se_4O_{12} (Mijlhoff, 1965). These results, limited in number and accuracy, indicate the need for further determinations of selenate structures in order to improve the understanding of bonding in tetrahedral oxyanions.

The lattice parameters of K_2SeO_4 were originally determined by Koch-Holm & Schönfeldt (1927). In their description of the orthorhombic K_2CrO_4 , Zachariassen & Ziegler (1931) listed K_2SeO_4 as one of several crystals isomorphous with β - K_2SO_4 . This was confirmed by Gattow (1962) who deduced the space group $Pnam$, in agreement with that of β - K_2SO_4 (Robinson, 1958).

Experimental

The crystals of K_2SeO_4 obtained from the aqueous solution of a BDH‡ product evaporated slowly at room temperature were thin, but rather large plates. From one of these plates an almost cylindrical needle, 0.8 mm long with an average diameter of 0.1 mm was carefully shaped. In terms of the axes chosen by Gattow (1962) the needle axis is a . K_2SeO_4 crystals, similarly to

others which have a β - K_2SO_4 type of structure (Sasvári, 1963), show an almost hexagonal pseudo-symmetry, with $b:c=1.7437 \simeq \sqrt{3}$. Thus care was needed to get the correct crystal orientation on the four-circle goniometer. For the correct orientation, according to the $0kl$ Weissenberg diagram, the intensity of the 080 reflexion should be considerably higher than that of 044, which corresponds to 080 in the pseudo-unit cell.

Data were collected on a Hilger & Watts automatic four-circle diffractometer in the equi-inclination arrangement. Integrated intensities were measured for $\theta \leq 56^\circ$ by the $\theta-2\theta$ scanning method using $Cu K\alpha$ radiation and a scintillation counter with an Ni filter and pulse height discrimination. Each reflexion was integrated in eighty steps of 0.01° . In consequence of a slight, but systematic error in the geometry of the four-circle goniometer, which could not be completely eliminated, the $hk0$ reflexions had to be remeasured with a revised orientation matrix. The observed structure factors were derived from the integrated intensities in a data reduction program, which also corrected for the variation in the integrated intensity of a standard reflexion (111) measured at frequent intervals during the data collection. Correction was made for absorption ($\mu R=1.3$) by the method described for cylindrical crystals in *International Tables for X-ray Crystallography* (1962). 362 independent reflexions were measured, of which 14 were below threshold and have not been included in the refinement. The lattice parameters given by Gattow (1962) were refined from measurement of diffraction angles on the diffractometer.

Crystal data

K_2SeO_4 . $M=221.15$. Orthorhombic $a=7.661 \pm 0.004$,
 $b=10.466 \pm 0.008$, $c=6.003 \pm 0.003$ Å;
 $V=481.32$ Å³, $Z=4$, $D_c=3.052$ g. cm⁻³,
 $D_x=3.032$ g. cm⁻³, $F(000)=416$.
Space group $Pnam$ (no. 62).
 μ for $Cu K\alpha$ ($\lambda=1.5418$ Å) 263.7 cm⁻¹.

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Table 3. *Vibration parameters with their e.s.d.'s (Å²)*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Se	0.0125 (11)	0.0160 (10)	0.0172 (10)	-0.0006 (4)	0	0
K(1)	0.0164 (19)	0.0295 (17)	0.0283 (16)	0.0032 (11)	0	0
K(2)	0.0135 (15)	0.0198 (15)	0.0264 (16)	0.0002 (11)	0	0
O(1)	0.0474 (43)	0.0417 (36)	0.0239 (35)	0.0132 (31)	0.0060 (31)	-0.0107 (31)
O(2)	0.0373 (70)	0.0213 (49)	0.0465 (60)	-0.0090 (41)	0	0
O(3)	0.0389 (83)	0.0583 (75)	0.0584 (72)	-0.0088 (52)	0	0

Table 4. *Interatomic distances and bond angles for the SeO₄ group*

	Uncorrected	Corrected	
Se-O(1)	1.628 Å	1.649 (6) Å	
Se-O(1')	1.628	1.649 (6)	
Se-O(2)	1.625	1.644 (9)	
Se-O(3)	1.622	1.648 (16)	
O(1) ··· O(1')	2.676 (9) Å	O(1)-Se-O(1')	110.50 (0.37)°
O(1) ··· O(2)	2.640 (10)	O(1)-Se-O(2)	108.43 (0.33)
O(1) ··· O(3)	2.660 (15)	O(1)-Se-O(3)	109.84 (0.34)
O(1') ··· O(2)	2.640 (10)	O(1')-Se-O(2)	108.43 (0.33)
O(1') ··· O(3)	2.660 (15)	O(1')-Se-O(3)	109.84 (0.34)
O(2) ··· O(3)	2.656 (19)	O(2)-Se-O(3)	109.76 (0.59)

1961). The calculations were performed on the ATLAS computer using a program written by J. S. Stephens. The corrections to the bond lengths are quite considerable, ranging from 0.019 to 0.026 Å. Table 4 gives the uncorrected and corrected bond lengths, the oxygen-oxygen distances and the bond angles with their estimated standard deviations. The uncorrected potassium-oxygen distances are given in Table 5.

Table 5. *Potassium-oxygen interatomic distances*

The coordinates are given in accordance with the parameters shown in Table 2 and Figs. 1 and 2.

K(1) (x, y, z)	...		
O[I]	O(1)	(x, y, z)	3.20 Å
O[II]	O(1)	(x, y, $\frac{1}{2}-z$)	3.20
O[III]	O(1)	($-\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$)	3.26
O[IV]	O(1)	($-\frac{1}{2}+x$, $\frac{1}{2}-y$, z)	3.26
O[V]	O(1)	($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}+z$)	3.00
O[VI]	O(1)	($\frac{1}{2}-x$, $-\frac{1}{2}+y$, -z)	3.00
O[VII]	O(2)	($-\frac{1}{2}+x$, $-\frac{1}{2}-y$, $\frac{1}{2}-z$)	3.23
O[VIII]	O(2)	($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}+z$)	3.02
O[IX]	O(2)	($\frac{1}{2}-x$, $\frac{1}{2}+y$, -z)	3.02
O[X]	O(3)	($\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$)	2.64
O[XI]	O(3)	(x, y, z)	3.76
K(2) (x, 1+y, z) ...			
O[XII]	O(1)	(-x, -y, -z)	2.83 Å
O[XIII]	O(1)	(-x, -y, $\frac{1}{2}+z$)	2.83
O[V']	O(1)	($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}+z$)	2.73
O[VII']	O(1)	($\frac{1}{2}-x$, $\frac{1}{2}+y$, -z)	2.73
O[XIV]	O(2)	(x, 1+y, z)	2.80
O[VII']	O(2)	($-\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$)	2.79
O[XI]	O(3)	(x, y, z)	2.98
O[XV]	O(3)	(-x, -y, -z)	3.32
O[XVI]	O(3)	(-x, -y, $\frac{1}{2}+z$)	3.32

Discussion

The two kinds of potassium ion have different environments (Table 5 and Figs. 1 and 2). K(1) is surrounded by 11 oxygen atoms. One of them is at a

rather long distance (3.76 Å) but geometrically it seems to belong to the environment of K(1). This oxygen atom, O[XI], and two others, O[VII] and O[X], form an almost regular triangle (O[VII]-O[X]=5.44, O[VII]-O[XI]=5.47, O[X]-O[XI]=5.30 Å) around the potassium ion on the common mirror plane at $z=\frac{1}{4}$. The other eight oxygen atoms form two mirror-related irregular tetrahedra surrounding the potassium ion. The planes formed by O[II], O[III] and O[V] and by O[I], O[IV] and O[VI] are almost parallel to the mirror plane ($\epsilon=4.5^\circ$), while the fourth members of these tetrahedra, O[IX] and O[VIII], are almost above and under the potassium ion at distances of $z=\pm 0.5$. Thus the 11 oxygen atoms form a nearly spherical environment for K(1). The other potassium ion K(2) has only 9 oxygen atoms in its neighbourhood. Three oxygen atoms, O[VII'], O[XI] and O[XIV], share the mirror plane with K(2), while three, O[V'], O[XIII] and O[XV], are above and three, O[VI'], O[XII] and O[XVI] are below in a rather irregular arrangement. The average potassium-oxygen distance of 2.93 Å for K(2) is significantly shorter than the average of 3.14 Å for K(1).

The SeO_4^{2-} anion is an almost regular tetrahedron within e.s.d.'s. The mean value of the vibrationally corrected Se-O bond lengths is 1.648 ± 0.010 Å. This is in a good agreement with the mean value in $\text{Cu}(\text{NH}_3)_2\text{SeO}_4$, which was originally given by Morosin (1969) as 1.635 ± 0.008 Å but increases to 1.643 Å on vibrational correction. A similar but less accurate value of 1.654 ± 0.021 Å was found in Na_2SeO_4 (Kálmán & Cruickshank, 1969; Náray-Szabó & Argay, 1963). In Se_4O_{12} (Mijlhoff, 1965) the Se-O distances involving the bridging oxygen atoms are 1.75 and 1.80, and for the non-bridging oxygen atoms 1.54 and 1.56 Å (e.s.d.'s. ≈ 0.013 Å); however the mean value of 1.66 Å is similar to those in the orthoselenates. The hypo-

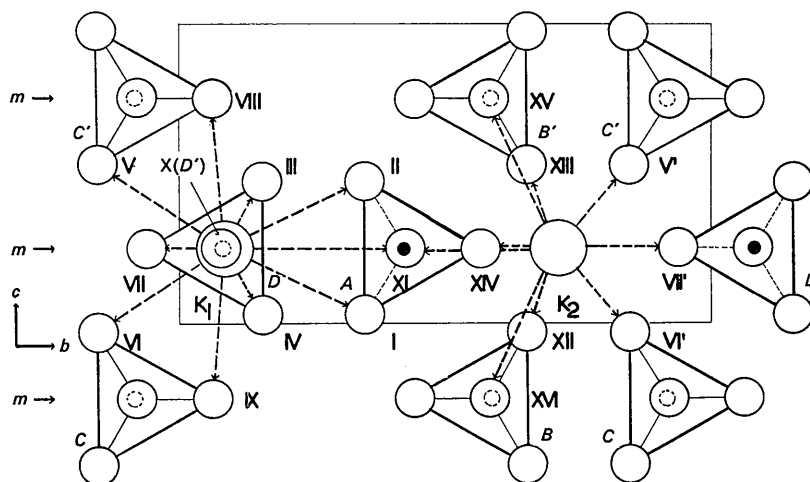


Fig. 2. Projection of the structure along [100]. See caption to Fig. 1 for explanations.

thetical Se–O single bond is presumably about 1.85 Å, which indicates that in the orthoselenates the Se–O bond has multiple-bond character.

In each orthoselenate the O–Se–O angles are close to the regular tetrahedral value, especially in $Cu(NH_3)_2SeO_4$, where the root-mean-square deviation is only 0.13° .

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